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# Raman scattering in electronically excited $C_{60}$

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The low-temperature Raman spectrum of $2a_0$-fcc single crystal $C_{60}$ recorded using low-irradiance 514 nm excitation shows only a single peak in the region of the 1468 $cm^{-1}$ out-of-phase ring mode. For higher irradiances a new broad peak appears in the spectrum at a somewhat lower frequency. Simultaneously, an increase of the luminescence is observed. As the irradiance increases the new peak gains intensity and shifts to lower frequencies, whereas the original peak slowly disappears. It is argued that this peak originates from electronically excited $C_{60}$. A simple electronic four-level model is proposed to explain the observed effects.

Buckminsterfullerene ($C_{60}$), the related fullerenes and their derivatives have proved to be an exciting field of research [1,2]. The development of an efficient method to produce these new forms of carbon in macroscopic quantities [3] made it possible to study not only the molecular, but also the solid-state properties of the fullerenes. The high symmetry of the prototype $C_{60}$ makes this molecule an interesting representative. The $I_h$ symmetry leads to the peculiar rotational dynamics [4] in solid $C_{60}$. At room temperature the $C_{60}$ molecules have a large degree of rotational freedom, resulting in a cubic closest packing fcc structure. At $T \approx 255$ K the rotational freedom freezes and a first-order phase transition [5,6] to a simple cubic (sc) structure takes place. In this phase the molecules can still rachet between equivalent orientations. Finally, the low-temperature structure, in which the racheting has also frozen out, is $2a_0$-fcc [7,8].

The relatively small influence of the crystal field, the rotational–vibrational coupling in solid $C_{60}$ [9] and the electron–phonon interaction [10] in superconducting alkali-intercalated $C_{60}$ make the vibrational dynamics of solid $C_{60}$ of special interest. The vibrational properties of $C_{60}$ have been studied both theoretically [2,11] and experimentally [2,3,12–14]. Raman spectroscopy has proved to be a convenient method to study the solid-state vibrational properties of $C_{60}$ and related compounds [9,10]. It is well known that for 514 nm radiation, the wavelength used in most Raman experiments, the optical absorption is large due to electronic transitions and correspondingly the phonon modes are resonantly enhanced. In this Letter, we report detailed studies of the intensity and position of the $A_g$ modes as a function of the excitation power density. The results indicate that already for relatively low radiation intensities $C_{60}$ is excited to a metastable triplet state, with an associated softening of the dominant $A_g$ modes.

The crystals used in the experiments are sublimably grown from high-purity $C_{60}$ powder. The high quality of the single crystals has been checked by mass spectrometry, electron diffraction, electron microscopy and X-ray diffraction. Details of the $C_{60}$ production, the growth procedure and the quality analysis have been published elsewhere [15]. The crystals were removed from their quartz growth tubes and immediately (within a few minutes) mounted on the cold finger of a flow cryostat (stabilization $\pm 0.2$ K, calibrated to $\pm 2$ K), which was subsequently evacuated to $P \approx 5 \times 10^{-6}$ mbar. In this way the effect of contamination with oxygen can be kept to a minimum. Unpolarized Raman spectra of single-crystal $C_{60}$ have been recorded as a function of the irradiance using a DILOR XY multichannel Raman spectrometer (spectral slit width 1.5 $cm^{-1}$) in a backscattering geometry. An $Ar^+$ ion laser (514.5 nm, fo-

cused to 30 μm on a natural surface of solid $C_{60}$) has been used as excitation source. The Raman spectra did not differ for different randomly chosen spot positions on the crystal. High irradiances easily cause optical damage to the crystals, so a low-irradiance (2 W/cm$^2$, total laser power 15 μW) spectrum has been recorded after each measurement. No detectable changes have been noticed in these low-irradiance spectra, as is shown by the dotted curves in fig. 1 (recorded at 5 W/cm$^2$). Only after exposure to very high irradiances ($>500$ W/cm$^2$) did the spectra change irreversibly, indicating optical damage to the crystals.

Fig. 1 shows three typical Raman spectra of the out-of-phase $A_g$ ring mode region recorded at $T=40$ K using (a) 5 W/cm$^2$, (b) 110 W/cm$^2$ and (c) 370 W/cm$^2$ irradiance (solid lines). The dashed lines in fig. 1 are fits of one ((a) and (c)) or two (b) Lorentzian shaped peaks to the data. For low irradiance (spectrum (a)) we observe the ground-state $A_g$ out-of-phase ring mode of the $C_{60}$ molecule, with a center frequency $\omega_0=1468$ cm$^{-1}$ and a full width at half maximum (fwhm) of 3 cm$^{-1}$. For moderate irradiance (50 W/cm$^2 \leqslant P \leqslant 300$ W/cm$^2$) a new broad (fwhm = 8 cm$^{-1}$) peak appears in the spectrum, initially centered at 1465 cm$^{-1}$. Simultaneously, the coexisting original $A_g$ mode, which remains at the same position with approximately the same width loses intensity, i.e., spectral intensity is transferred to the new modes. For irradiances exceeding 300 W/cm$^2$ the original $A_g$ mode has completely vanished and a further broadening and softening is observed. In fig. 2 we have plotted the peak intensity ratio of the ground-state mode to the extra modes $I_{gr}/I_{exc}$, showing a gradual shift of oscillator strength with increasing irradiance. The inset shows the center positions of the modes as a function of the irradiance. It is clear that there is no continuous shift of the phonon modes, but rather a gradual appearance of distinct new modes. At an irradiance of approximately 300 W/cm$^2$ a quasi-discontinuous transition occurs and only a single broadened peak is observed.

The appearance of the new modes in the spectrum

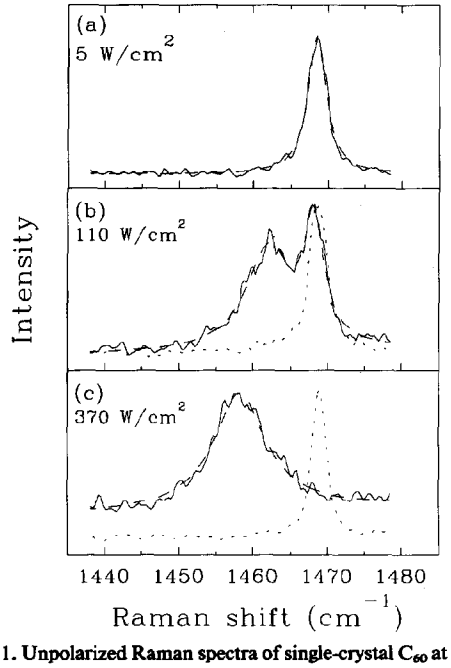


Fig. 1. Unpolarized Raman spectra of single-crystal $C_{60}$ at $T=40$ K showing the region of the $A_g$ out-of-phase ring mode (solid lines). The spectra have been recorded using 514 nm excitation with an irradiance of (a) 5 W/cm$^2$, (b) 110 W/cm$^2$ and (c) 370 W/cm$^2$. The dotted lines in (b) and (c) show the spectra recorded immediately after recording the high-irradiance spectra on the same spot at 5 W/cm$^2$. The dashed lines are fits of Lorentzian-shaped peaks to the data.

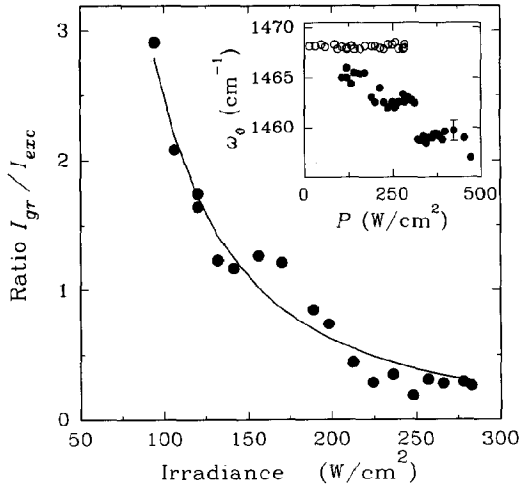


Fig. 2. Ratio of the peak intensities of the 1468 cm$^{-1}$ $A_g$ mode and the new modes as a function of the irradiance at $T=40$ K (dots). The solid line shows a fit of an inverse square irradiance dependence to the data (see text). The inset shows the irradiance dependence of the frequency of the 1468 cm$^{-1}$ peak (open circles) and the additional modes (closed circles).

is accompanied by an increase of the "background" intensity. The irradiance dependence of this intensity (taken at 540 nm), which originates from luminescence processes, is plotted in fig. 3 (dots). The overall behavior is an increase of the luminescence upon increasing irradiance. Superimposed on this behavior steps in the luminescence can be observed, which coincide with discontinuous changes of the frequency of the additional mode.

The observed changes in the spectra induced by the high irradiance are completely reversible. No changes have been observed in the low-irradiance spectra recorded immediately after the recording of the high-irradiance spectra. This instantaneous reversibility together with the increasing luminescence and the relatively strong absorption of 514 nm radiation in $C_{60}$ is a strong indication that the new peaks in the spectra are vibrational modes of electronically excited $C_{60}$ corresponding to the 1468 $cm^{-1}$ $A_g$ out-of-phase ring mode of the ground-state molecule. The lower frequency of the new modes is consistent with this interpretation; being a full-shell system, any excited state of $C_{60}$ is an anti-bonding state, and will have weaker intra-molecular forces. In view of this picture, the peak intensity ratio of the normal $A_g$ mode ($I_{gr}$) to the new mode ($I_{exc}$) should give a good measure for the ratio of the number of molecules in the ground state to those which are excited.

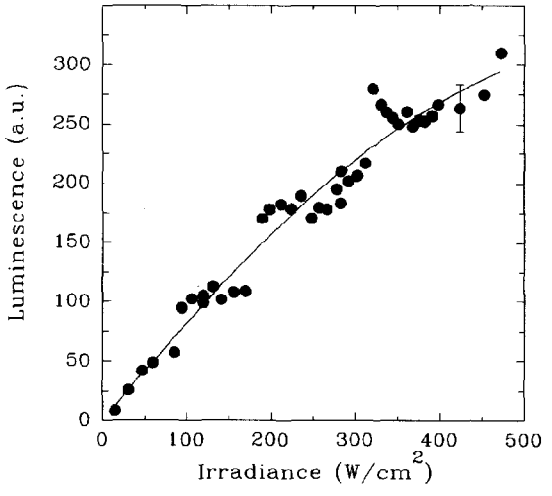


Fig. 3. Luminescence signal at 540 nm as a function of the irradiance. The solid line is a fit to $1/(1+\mathscr{R})$ with $\mathscr{R} \propto I^2$.

It should be noted that for low irradiance, when the new mode is not yet observable, the total $A_g$ intensity increases linearly with the irradiance. For higher irradiance, this linear increase changes to a monotonic decrease of the total $A_g$ intensity, which includes the new mode now. This behavior points to a strong irradiance dependence of the optical penetration depth of the 514 nm radiation field, caused by optically induced electronic transition processes in the excited $C_{60}$ molecules. In addition one may expect a change in the resonance conditions leading to a decrease of the resonant enhancement [16] of the Raman modes. Also differences in the Raman cross section for the ground state and excited molecules may play a minor role here. Clearly, changes of the penetration depth or the cross section do not influence the irradiance dependence of $I_{gr}/I_{exc}$. Note that none of the effects described above are observed in Raman spectra recorded using 740 nm (1.67 eV) excitation [17], an energy below the $S_0$–$T_0$ energy gap [18], for which optical excitations are expected to be of minor importance.

To understand the observed effects in the irradiance dependence of the Raman spectrum we propose the following qualitative model. Consider the simplified energy level diagram for the electronic structure of $C_{60}$ depicted in fig. 4. The left part of the diagram shows the electronic ground state ($|1\rangle$, $h_u$ symmetry) and an excited singlet state ($|2\rangle$, $t_{1u}$ symmetry). Optical transitions between these two states are first-order forbidden. The (weak) appearance of this transition in absorption spectra [18,19] indicates, however, that this transition is vibroni-

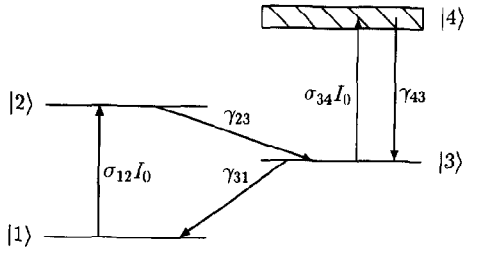


Fig. 4. Simplified electronic energy level diagram for $C_{60}$. The arrows indicate the most important electronic transitions in the presence of a 514 nm radiation field.

cally allowed. The level $|3\rangle$ in the right part of the diagram represents the triplet ($t_{1_g}$ or $t_{2_g}$ symmetry) level that is populated by inter-system crossing $|2\rangle \rightarrow |3\rangle$, with a rate $\gamma_{23}$. The band of levels $|4\rangle$ schematically represents the various electronic states that can be populated with one additional photon, starting from state $|3\rangle$. The arrows in fig. 4 indicate the most important stimulated absorption processes ($\sigma_{ij}I_0$, where $\sigma$ is the absorption cross section and $I_0$ the photon flux) and (non)-radiative emission processes ($\gamma_{ij}$) between the various levels. Only the relevant processes are shown. The cross section for absorption of 514 nm radiation by ground-state $C_{60}$ molecules is [18] $\sigma_{12} \approx 2.5 \times 10^{-18}$ cm$^2$. After singlet excitation, an efficient inter-system crossing to the lowest triplet state takes place with $\gamma_{23} = 3 \times 10^{10}$ s$^{-1}$ [20]. Groenen et al. measured the lifetime of the triplet states at 1.2 K using pulsed EPR experiments in an initially nearly fully triplet-state excited single crystal of $C_{60}$ to be approximately 0.4 ms [21,22]. This long lifetime leads to the conclusion that there is no efficient path for decay of triplet excited molecules to the singlet ground state. Specifically, triplet–triplet annihilation which is neglected in the model (justified by the long triplet lifetime) and which can be important in molecular crystals, is of minor importance in solid $C_{60}$. From a rate equation including triplet–triplet annihilation one estimates that the rate for this decay channel is of the order of $10^{-18}$ s$^{-1}$, about 8 orders of magnitude less than the values usually found in molecular crystals. The absorption cross section in the triplet state is about one order of magnitude larger than $\sigma_{12}$ [23].

Of present interest is the ratio $\mathscr{R}$ of the population of the ground state to the total population of the excited levels. Given the model of fig. 4, the steady-state populations of the excited levels relative to that of the ground state are

$$\frac{N_2}{N_1} = \frac{\sigma_{12}}{\gamma_{23}} I_0, \quad \frac{N_3}{N_1} = \frac{\sigma_{12}}{\gamma_{31}} I_0, \quad \frac{N_4}{N_1} = \frac{\sigma_{12}\sigma_{34}}{\gamma_{31}\gamma_{43}} I_0^2 .$$

Using these relations, the ratio $\mathscr{R}$ is

$$\mathscr{R}(I_0) = \left[\frac{\sigma_{12}}{\gamma_{31}} I_0 \left(1 + \frac{\gamma_{31}}{\gamma_{23}} + \frac{\sigma_{34}}{\gamma_{43}} I_0\right)\right]^{-1}$$

$$\approx \left[\frac{\sigma_{12}}{\gamma_{31}} I_0 \left(1 + \frac{\sigma_{34}}{\gamma_{43}} I_0\right)\right]^{-1}, \qquad (1)$$

where the approximation $\gamma_{31}/\gamma_{23} \ll 1$ is used. Note that for low irradiance the ratio of electronically excited molecules is proportional to $\sigma_{12}I_0/\gamma_{31}$. At 40 W/cm$^2$, $\sigma_{12}I_0/\gamma_{31} \approx 0.1$ and indeed the new line starts to appear for this irradiance. For values lower than 40 W/cm$^2$ one expects to observe the ground-state vibrations in Raman spectroscopy, while for substantially higher irradiance the spectrum of electronically excited $C_{60}$ ($C_{60}^*$) is observed.

Now consider the Raman intensity ratio of fig. 2 again. The data in this figure can be satisfactorily fit to an inverse square irradiance dependence (solid line). The frequency of the new $C_{60}^*$ mode in the Raman spectrum shows a weakening upon increasing laser power (see inset fig. 2). This may be related to further excitations into the triplet manifold, in line with the reported limiting optical properties of $C_{60}$ [24], and with the broad fwhm of the $C_{60}^*$ peak in the Raman spectra. However, since the results presented here are obtained from a continuous wave experiment this is only possible if more triplet levels have a relatively long lifetime. It would therefore be interesting to perform pulsed Raman experiments to obtain more insight into the vibrational properties and the lifetimes of electronically excited $C_{60}$. The luminescence is expected to be proportional to the fraction of molecules that is excited into the triplet manifold. This fraction is equal to $1/(1+\mathscr{R})$. A fit of this relation, using the $\mathscr{R} \propto I^2$ dependence, to the luminescence data of fig. 3 yields a satisfactory result.

It is known that in the presence of oxygen the triplet state of $C_{60}$ is efficiently quenched and $\gamma_{31}$ increases by orders of magnitude [25]. So in a way, removing oxygen from the sample (thereby decreasing $\gamma_{31}$) has the same effect as increasing the irradiance, as only the ratio $\sigma_{12}I_0/\gamma_{31}$ is important. This led to the erroneous conclusion [26,27] that the 1468 cm$^{-1}$ mode is oxygen-induced and that the real $C_{60}$ mode has a lower frequency, as it appeared in the spectra of oxygen-free samples. It can now be concluded that this lower-frequency mode originates from electronically excited $C_{60}^*$. In in-situ experiments [28] with a total absence of oxygen one expects that $\gamma_{31} \ll 2.5 \times 10^3$ s$^{-1}$, leading to an appreciable triplet state population even at low irradiance.

The observed changes in the 1468 cm$^{-1}$ region are not the only effects originating from triplet excited $C_{60}$. For the in-phase $A_g$ mode is similar behavior

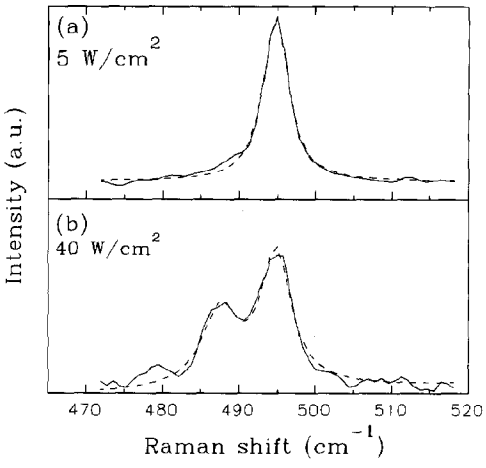


Fig. 5. Unpolarized Raman spectra of single crystal $C_{60}$ at $T=300$ K showing the region of the $A_g$ in-phase ring mode (solid lines). The spectra have been recorded using 514 nm excitation with an irradiance of (a) 5 W/cm$^2$, (b) 40 W/cm$^2$. The dashed lines are fits of Lorentzian-shaped peaks to the data.

has been observed, i.e. the appearance of a new mode at a somewhat lower frequency. This is illustrated in fig. 5, where the in-phase $A_g$ mode region recorded at $T=300$ K is shown for (a) 5 W/cm$^2$ and (b) 40 W/cm$^2$. In the fcc phase, the triplet-state excitations become important at low irradiances. Apart from the activation of the new modes in the spectra, this results in line-shape changes of the $H_g$ squashing mode (not shown) which is at present not well understood. The fact that in the fcc phase the triplet state is much more easily produced might add to the discontinuous changes of Raman spectra observed at the rotational ordering transition [9].

In summary, we have presented a Raman study of the vibrational properties of single-crystal $C_{60}$ in the excited state, concentrating on the $A_g$ out-of-phase ring mode. The irradiance dependence of the spectra can be explained in terms of a simple four-level model for the electronic structure of $C_{60}$. For low irradiances only a single peak is observed which is assigned to the $A_g$ mode of ground-state $C_{60}$, rather than to an oxygen-induced mode.

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